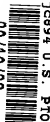


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Attorney Docket No.: TS0926 (US)
 A Named Inventor/Application Identifier: Maria B. H. Van Crijnen-Beers, Jean-Paul
 Darnaville, Carolus M. A. M. Mesters, and Thomas J. Remans
 Express Mail Label No.: EL2813743SUS
 Title: METHOD FOR PREPARING A CATALYST
 Date: September 18, 2000



UTILITY PATENT APPLICATION TRANSMITTAL
UNDER 37 CFR 1.53(b)

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1. ☒ This application is a(n):
 - a. ☒ Original
 - b. ☐ Continuation-in-part of Application Serial No. _____ filed _____
 - c. ☐ Divisional of Application Serial No. _____ filed _____
☐ Applicant(s) elect the invention of Group/Species _____
 - d. ☐ Continuation of Application Serial No. _____ filed _____
2. ☒ Specification
 - a. ☒ Pages 17
 - b. ☐ Drawing, Total sheets _____
3. ☐ Oath or Declaration
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☐ Please delete the following named inventors in the prior application: _____
4. ☐ Please amend the specification
 - a. ☐ By inserting before the first line:
 This is a ☐ continuation ☐ division ☐ continuation-in-part of
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 This application claims the benefit of U.S. Provisional Application No.
 _____, filed _____, the entire disclosure of which is
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 - c. ☐ Cancel claims _____
5. ☒ This application claims the benefit of Application Number 99402401.6 filed on
September 27, 1999, in Europe under 35 U.S.C. § 119, § 365(a), or § 365(b).
 (For originals)
6. ☐ Microfiche Computer Program (Appendix)
7. ☐ Recognize as an associate attorney _____, Registration No. _____

8. ☒ Address all future communications to:

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9. ☒ Fee Transmittal (duplicate enclosed)

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TOTAL CLAIMS (37 CFR 1.16(c))	16 - 20 =	0	X \$18.00 =	0
INDEPENDENT CLAIMS (37 CFR 1.16(b))	1 - 3 =	0	X \$78.00 =	0
MULTIPLE DEPENDENT CLAIMS (if applicable) (37 CFR 1.16(d))		0	+ \$260.00 =	0
			BASIC FEE (37 CFR 1.16(a))	\$690.00
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Respectfully submitted,

MARIA B. H. VAN CRIJNEN-BEERS,
JEAN-PAUL DARNVILLE,
CAROLUS M. A. M. MESTERS,
and THOMAS J. REMANS

By 
Their Attorney, Yukiko Iwata
Registration No. 35,748
(713) 241-5593

P. O. Box 2463
Houston, Texas 77252-2463

METHOD FOR PREPARING A CATALYST

5 The invention relates to a method for preparing a catalyst comprising a zeolite and a low acidity refractory oxide binder which is essentially free of alumina.

10 Such a method is described in patent publication US-A-5053374 which illustrates the preparation of a silica-bound USY catalyst. In this preparation 65 weight parts of the zeolite in the form of a powder was mixed with 35 weight parts of silica consisting of various ratios of an amorphous
15 precipitated silica (PPG Industries HiSil 233 EP) and a basic colloidal silica of the type Ludox HS-30. A homogenous mix was obtained by mulling. The moisture content of the mix was adjusted to 42-47 weight percent with deionized water. The mix was extruded to
20 yield an extrudate. The extrudates were subsequently dried and ammonium exchanged to remove sodium and subsequently calcined.

25 When contents of binder and zeolite are used in the context of the present invention the content on a dry basis is meant. When a pH value is mentioned the pH as measured in water of 18 °C is meant.

30 There remains room to improve the strength of the catalyst extrudates as obtained by the process as described in US-A-5053374. This is especially true when catalyst extrudates are made having a zeolite content of below 50 wt%. It appears that the strength of the catalyst is negatively influenced when the

zeolite content is reduced. For some applications a zeolite content of well below 50 wt% is advantageous in terms of improved selectivity and activity of the catalysed reaction. An example of such an application is the catalytic dewaxing process as described in WO-A-200029511.

The object of the present invention is a process to prepare a low acidity refractory oxide bound zeolite catalyst having a high crushing strength. A further object is to provide a process which enables one to prepare silica bound catalysts of sufficient strength having a zeolite content of below 50 wt%.

The object of the invention is achieved by the following process. A method for preparing a catalyst comprising a zeolite and a low acidity refractory oxide binder which is essentially free of alumina which method comprises:

- (a) preparing an extrudable mass comprising a substantially homogenous mixture of zeolite, water, a source of the low acidity refractory oxide binder present as an acid sol and an amine compound,
- (b) extruding the extrudable mass resulting from step (a),
- (c) drying the extrudate resulting from step (b); and,
- (d) calcining the dried extrudate resulting from step (c).

Catalyst particles obtained by the above process have an increased crushing strength. This is advantageous because such catalysts are typically applied in a packed bed reactor. Due to the normally

high operating pressure and mass flows in the reactor strong catalyst particles are advantageous.

Examples of the low acidity refractory oxide binder material which is essentially free of alumina are silica, zirconia, titanium dioxide, germanium dioxide, boria and mixtures of two or more of these like for example silica-zirconia and silica-titania. A preferred binder is silica. The description of the invention will further refer to a silica binder only. It will be understood that the below preferred conditions will, when applicable, also apply to other possible binders as here described.

The acid silica sol may be any colloidal silica having a pH lower than 7. An example of a suitable acid silica sol is Nyacol 2034DI which can be obtained from PQ Corp, Valley Forge, Pennsylvania or Ultra-Sol 7H from RESI Inc, Newark. The surface of the acid silica sol particle comprises -OH groups. It is believed that for obtaining a catalyst particle having a sufficient strength it is essential that during the mixing of the components in step (a) some or all of these groups are converted to -O⁻ groups. This is achieved by adding the amine compound in step (a). It has further been found that when adding the amine compound just before performing step (b) an even more stronger catalyst particle is obtained. It is believed, although we do not wish to be bound to this theory, that the stronger catalyst is obtained because not all of the -OH groups on the sol particle surface are converted into -O⁻ groups. Thus step (a) is preferably performed by first mixing the zeolite and the acid silica sol into a first homogeneous

mixture and subsequently adding the amine compound to the first homogeneous mixture such that the pH of the resulting second mixture is raised from below 7 to a value of above 8. It can be easily determined by one skilled in the art, by straightforward experimentation, what the optimal moment in step (a) is for adding the amine compound. As a guideline it is preferred to add the amine compound during the second half of the time and more preferably in the last quarter of the time required to mix the components in step (a). Most preferably the amine compound is added within 20 minutes before performing step (b).

The extrudable mass in step (a) should have a sufficient viscosity in order to be extruded into shapes. One skilled in the art will know how to achieve such a paste like mixture. For example by adding water in step (a) the viscosity can be lowered. The water content of the sol may be between 60 and 80 wt%. Preferably the water content of the extrudable mass as obtained in step (a) does not exceed 60%, and preferably is at least 35% by weight.

When preparing catalysts having a lower zeolite content, especially lower than 50 wt%, it becomes more difficult to achieve a sufficient high viscosity and preferably some of the acid silica sol is replaced by silica powder as the silica source. To obtain the strongest catalysts it is preferred to maximise the amount of acid silica sol used relative to the amount of silica powder used, while still achieving a sufficient viscosity of the extrudable mass. The optimal amount of silica powder to be used

will depend on the zeolite content, wherein at a low zeolite content of the catalyst, more silica powder will have to be used. One skilled in the art can easily determine the optimal composition in view of the above teaching. The silica powder may be commercially obtained silica powder, for example Sipernat 22 or 50 (as obtained from Degussa AG), Nasilco Ultrasil VN3SP or HiSil 233 EP from PPG Industries. The solid silica powder particles preferably have a mean diameter of between 10 μm and 200 μm .

The amine compound is preferably a compound according to the general formula $\text{R}^1\text{R}^2\text{R}^3\text{N}$ in which R^1 - R^3 may be hydrogen and/or an alkyl group having 1-6 carbon atoms. Examples are ammonia, methyl ethyl amine, triethyl amine, of which ammonia, is the most preferred. The amine compound should preferably be added in such an amount in order to raise the pH of the mass to alkaline conditions. Preferred conditions are a pH of the mixture obtained in step (a) of above 8. The pH will be lower than 14.

Step (a) may for example be performed at ambient conditions by first mixing the zeolite, optionally the silica powder and acid silica sol, subsequently adding an amine compound and optionally at the end of step (a) a plasticising agent. The plasticiser agent is used to increase the viscosity of the mixture in order to obtain an extrudable mass. Suitable plasticising agents are for example dextrose, gelatine, glucose, glues, gums, salts, waxes, starch and cellulose ethers. Some typical cellulose ether binders are methylcellulose, ethylhydroxy

ethylcellulose, hydroxybutyl methylcellulose,
hydroxymethylcellulose, hydroxypropyl
methylcellulose, hydroxyethyl methylcellulose,
hydroxybutylcellulose, hydroxyethylcellulose,
5 hydroxypropylcellulose, sodium carboxy
methylcellulose, and mixtures thereof.
Methylcellulose and/or methylcellulose derivatives
are especially suited as organic binders in the
practice of the present invention with
10 methylcellulose, hydroxypropyl methylcellulose, or
combinations of these being preferred. Preferred
sources of cellulose ethers are Methocel A4M, F4M,
F240, and K75M from Dow Chemical Co.

The extrusion in step (b) may be performed by
15 well known processes as for example illustrated in
Perry's Chemical Engineers' Handbook, McGRAW-HILL
International Editions, sixth edition, 1984, p 8-60
to 8-66 and in Particle Size Enlargement, Handbook of
powder Technology Vol. 1, Elsevier, 1980, p 112-121.
20 Examples of such methods are extrusion performed by a
screw extruder, a plate or ram extruder. The
extrudates can have a wide variety of forms and
sizes.

Drying step (c) and calcining step (d) may be
25 performed under conditions well known to one skilled
in the art. Step (c), for example, may take place at
a temperature of at least 60 °C to about 250 °C, for
a time sufficient to dry the extrudate, for example,
for at least 1 hour. Calcining step (d), for example,
30 may take place in air, or other inert gas, at
temperatures ranging from 250 °C to 850 °C for

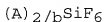
periods of time ranging, for example, from about 1 to about 48 hours or more.

The method of preparing a low acidity refractory oxide-bound zeolite of this invention is not limited to any particular zeolite and in general includes all metallosilicates, particularly the aluminosilicates whether or not previously dealuminized to increase the framework silica:alumina ratio. Typical zeolites include ZSM-4 (Omega), ZSM-5; ZSM-11, ZSM-12, ZSM-20, ZSM-22, ZSM-23, ZSM-35, ZSM-48, ZSM-50, Beta, X, Y and L as well as ferrierite and mordenite.

Catalysts of improved selectivity and other beneficial properties can be obtained by subjecting the catalyst extrudates to a dealumination treatment. Dealumination can be attained by methods known in the art, such as for example acid leaching or by a steam treatment. Steam treatment is effected by contacting the catalyst extrudates with steam at elevated temperatures ranging from about 250 °C to 650 °C and preferably from about 400 °C to 550 °C. The treatment can be accomplished in an atmosphere of 100% steam or in an atmosphere consisting of steam or ammonia and some other gas which is essentially inert to the zeolites. A similar treatment can be accomplished at lower temperatures and elevated pressure, e.g., from about 180 °C to 370 °C at from about 10 to about 200 atmospheres.

Particularly useful dealumination methods are those, wherein the dealumination selectively occurs, or anyhow is claimed to occur selectively, at the surface of the crystallites of the molecular sieve. Preferably dealumination is performed by a process in

which the zeolite is contacted with an aqueous solution of a fluorosilicate salt wherein the fluorosilicate salt is represented by the formula:



5 wherein 'A' is a metallic or non-metallic cation other than H⁺ having the valence 'b'. Examples of cations 'b' are alkylammonium, NH₄⁺, Mg⁺⁺, Li⁺, Na⁺, K⁺, Ba⁺⁺, Cd⁺⁺, Cu⁺, Ca⁺⁺, Cs⁺, Fe⁺⁺, Co⁺⁺, Pb⁺⁺, Mn⁺⁺, Rb⁺, Ag⁺, Sr⁺⁺, Tl⁺, and Zn⁺⁺. Preferably 'A' is the ammonium cation. The zeolite material may be contacted with the fluorosilicate salt in an amount of at least 0.0075 moles per 100 grams of the zeolite material. The pH is suitably between 3 and 7. An example of the above described dealumination process is described in US-A-5157191.

15 The original cations associated with each of the zeolites utilized herein can be replaced by a wide variety of other cations employing techniques well known in the art. Such a replacement of cations is suitably performed after the above described optional dealumination step. Typical replacing cations including hydronium, ammonium, alkyl ammonium and metal cations. Suitable metal cations include metals such as rare earth metals, as well as metals of Groups IIA and B of the Periodic Table, e.g., zinc, and Group VIII of the Periodic Table, e.g., platinum, palladium and nickel.

25 Typical ion-exchange techniques call for contacting the selected zeolite with a salt of the desired replacing cation. Although a wide variety of salts can be employed, particular preference is given

to chloride, nitrates and sulfates. Representative ion-exchange techniques are disclosed in a wide variety of patents including US-A-3140249, US-A-3140251 and US-A-3140253.

5 Following contact with a solution of the desired replacing cation, the catalyst is then preferably washed with water and dried and/or calcined as for example described above for step (c) and step (d).

10 The catalyst prepared by the method of this invention can find utility in a wide variety of processes which are both catalytic and non-catalytic. Quite obviously, the materials can be used as absorbents. Additionally, the materials can be used as catalysts for a wide variety of hydrocarbon
15 conversions. As is known in the art, a low acidity refractory oxide such as silica has low catalytic activity such that incorporation of a zeolite in the silica leads to some unusual effects. The low acidity refractory oxide can be used as a support for a
20 catalytic material, e.g., a hydrogenation component such as platinum, palladium, cobalt, molybdenum, iron, tungsten, nickel or mixtures of the same. In addition, the low acidity refractory oxide-bound zeolite extrudates find utility in hydrocracking,
25 isomerization, hydrogenation, dehydrogenation, polymerization, reforming, catalytic cracking, catalytic hydrocracking, toluene disproportionation, and the like. Thus, the extrudates of this invention can be used with or without added active metal
30 components for catalytic cracking, isomerization, alkylation, reforming and hydrogenative conversions such as hydrocracking, hydrogenation and hydrofining,

e.g., desulfurization and denitrogenation. In some types of hydrocarbon conversions, e.g., hydroprocessing, reforming, catalytic cracking and catalytic hydrocracking the use of a low-acidity refractory oxide-bound zeolites having lower levels of inherent activity than their alumina-bound counterparts can result in lower coke production and significant increases in cycle length.

Catalysts prepared by the process according to the invention can be advantageously used as dewaxing catalyst under well known catalytic dewaxing conditions in a process to prepare a lubricating base oil, a gas oil or as part of a hydrocracker process, which main products are middle distillates. Examples are described in WO-A-200029511, WO-A-200029512 and US-A-5804058 which are hereby incorporated by reference. Especially suitable are catalysts wherein the zeolite is ZSM-5, ZSM-12, ZSM-22, ZSM-23 or SZZ-32. More preferably the catalyst extrudate is subjected to a dealumination treatment as described above and even more preferably the zeolite is ion exchanged to incorporate a platinum, palladium or nickel metal. A preferred catalyst has a zeolite content of below 50 wt%. The lower zeolite level is preferably 10 wt%. Below this level the activity becomes too low for practical application of the catalyst.

The catalyst prepared by according to this invention may also be suitably be used in a xylene isomerisation process as for example described in US-A-5554274, US-A-4899011, US-A-5689027, US-A-5516956

and WO-A-9616005 which are hereby incorporated by reference.

The invention shall be illustrated by the following non-limiting examples.

5 Comparative Experiment A

On a dry basis, 60 weight parts of ZSM-5 (CBV8014 as obtained from Zeolyst International) were intimately admixed with 15 weight parts of amorphous precipitated silica powder (Sipernat-50 as obtained from Degussa) and with 25 weight parts of acid colloidal silica (Nyacol 2034DI as obtained from PQ Corporation); a homogenous mix was obtained by mulling. The total moisture content of the mix was adjusted to 55 weight percent with deionized water.

15 5 minutes before extruding the mixture a plasticiser agent, Methocel source (containing 2.1 wt% methocel), was added to the extrudable mass in a ratio of 7/100 of Methocel source relative to the zeolite dry mass. The mixture was extruded to yield cylinder extrudates with a diameter of 1.6 mm. The extrudates were subsequently dried at 120 °C for typically 2 hours in air and then calcined at 800 °C for 5 hours.

25 The Flat Plate Crushing Strength was measured by determining the force in N/cm at which the cylinder extrudate was crushed between two parallel flat plates. The cylinder extrudate was positioned between the plates in such that the cylindrical axis was parallel with the plates. This procedure was repeated 30 40 times and the average force at which crushing was observed was the resulting Flat Plate Crushing

Strength (FPCS). In this example a FPCS of 60 N/cm was measured. See also Table 1.

Comparative Experiment B

Comparative Experiment A was repeated except that the ZSM-5 content was 30 wt%, the silica powder content was 35 wt% and the acid silica sol content was 35 wt%. A FPCS of 86 N/cm was measured. As a result of the lower ZSM-5 content as compared to Comparative Experiment A one would expect a lower FPCS. The resulting higher FPCS is a result of the higher content of acid silica sol as compared to Comparative Experiment A. The FPCS is however not high enough for commercial application. A value of higher than 100 N/cm is desirable. See also Table 1.

Comparative Experiment C

Comparative Experiment B was repeated except instead of acid silica sol the same amount of basic colloidal silica of the type Ludox HS-30 was used. The Flat Plate Crushing Strength was 80 N/cm.

EXAMPLE 1

Comparative Experiment B was repeated except that, after mixing the ZSM-5, silica powder and acid colloidal silica, ammonia was added. Ammonia as a 2.5 wt% aqueous solution was added in a ratio of 1/12 ammonia solution relative to the zeolite dry mass. The resulting pH was 8.8. After adding the ammonia the mixing was continued for 35 minutes before extruding. The Flat Plate Crushing Strength was 122 N/cm. See also Table 1.

EXAMPLE 2

Example 1 was repeated except that ammonia was added after 35 minutes after mixing the ZSM-5, silica

powder and acid colloidal silica. After adding the ammonia the mixing was continued for 10 minutes before extruding. The Flat Plate Crushing Strength was 178 N/cm.

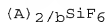
Table 1

Experi- ment	ZSM-5 con- tent (wt%)	Silica powder (wt%)	Silica sol (wt%)	acidity of used silica sol	ammonia added	FPCS (N/cm)
Comp. A	60	15	25	acid	no	60
Comp. B	30	35	35	acid	no	86
Comp. C	30	35	35	basic	no	80
Example 1	30	35	35	acid	35 minutes before extrusion	122
Example 2	30	35	35	acid	10 minutes before extrusion	178

WE CLAIM:

1. A method for preparing a catalyst comprising a zeolite and a low acidity refractory oxide binder which is essentially free of alumina comprising:
 - (a) preparing an extrudable mass comprising a substantially homogenous mixture of zeolite, water, a source of the low acidity refractory oxide binder present which comprises an acid sol, and an amine compound,
 - (b) extruding the extrudable mass resulting from step (a),
 - (c) drying the extrudate resulting from step (b); and,
 - (d) calcining the dried extrudate resulting from step (c).
2. The method of claim 1 wherein step (a) is performed by first mixing the zeolite and the acid sol into a first homogeneous mixture and subsequently adding the amine compound to the first homogeneous mixture such that the pH of the resulting second mixture is raised from below 7 to a value of above 8.
3. The method of claim 2 wherein the amine compound is added in step (a) within 20 minutes of performing step (b).
4. The method of claim 1 wherein the zeolite content, on a dry basis, is below 50 wt% as calculated on the finished catalyst and wherein the low acidity refractory oxide source used to prepare the extrudable mass in step (a) further comprises a powder of the low oxide refractory source.

5. The method of claim 1 wherein the low acidity refractory oxide binder is silica.
6. The method of claim 5 wherein the low acidity refractory oxide source used to prepare the extrudable mass in step (a) further comprises a powder of silica.
7. The method of claim 1 wherein the amine compound is ammonia.
8. The method of claim 1 wherein the zeolite is selected from the group consisting of ZSM-5, ZSM-12, ZSM-22, ZSM-23, and SZZ-32.
9. The method wherein the catalyst produced by the method according to claim 1 is subjected to a dealumination treatment.
10. The method according to claim 9 wherein the dealumination treatment is performed by a process in which the zeolite is contacted with an aqueous solution of a fluorosilicate salt wherein the fluorosilicate salt is represented by the formula:



wherein A is a metallic or non-metallic cation other than H⁺ having the valence b.

11. The method wherein a catalyst prepared by the method of claim 1 is subjected to a cation exchange treatment wherein a palladium, platinum or nickel metal is loaded on the catalyst.
12. A process for hydroprocessing a hydrocarbon feedstock comprising the steps of contacting said hydrocarbon feedstock with the catalyst produced according to the method of claim 1 at an elevated temperature and pressure optionally in the presence of hydrogen.

13. The process of claim 12 wherein the process is a catalytic dewaxing process.

14. The process of claim 12 wherein the process is a xylene isomerization process.

15. A hydroprocessing catalyst comprising a zeolite and a low acidity refractory oxide binder which is essentially free of alumina produced by the process of claim 1.

16. The hydroprocessing catalyst of claim 15 comprising a zeolite, a low acidity refractory binder which is essentially free of alumina and at least one Group VIII metal cation.

METHOD FOR PREPARING A CATALYST

5 Abstract of the Invention

A method for preparing a catalyst comprising a zeolite and a low acidity refractory oxide binder which is essentially free of alumina which method comprises:

- 10 (a) preparing an extrudable mass comprising a substantially homogenous mixture of zeolite, water, a source of the low acidity refractory oxide binder present which comprises an acid sol, and an amine compound,
- 15 (b) extruding the extrudable mass resulting from step (a),
- (c) drying the extrudate resulting from step (b); and,
- 20 (d) calcining the dried extrudate resulting from step (c).

DECLARATION AND POWER OF ATTORNEY FOR PATENT APPLICATION

ATTORNEY'S DOCKET NO.
TS0926 (US)

As a below named inventor, I hereby declare that:

My residence, post office address, and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled METHOD FOR PREPARING A CATALYST the specification of which is attached hereto unless the following box is checked:

☐ was filed on _____ as United States Application Number or PCT International Application Number _____ and was amended on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 27 CFR § 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

PRIOR FOREIGN APPLICATION(S)

APPLICATION NUMBER	COUNTRY	DAY/MONTH/YEAR FILED
09402401.6	Europe	27/09/99
APPLICATION NUMBER	COUNTRY	DAY/MONTH/YEAR FILED

Priority
Not Claimed

☐
☐

I hereby claim the benefit under 35 U.S.C. § 119(e) of any United States provisional application(s) listed below.

APPLICATION SERIAL NO.	FILING DATE
APPLICATION SERIAL NO.	FILING DATE

I hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s) or § 365(c) of any PCT International application designating the United States, listed below and insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

APPLICATION SERIAL NO.	FILING DATE	STATUS-PATENTED, PENDING, ABANDONED
APPLICATION SERIAL NO.	FILING DATE	STATUS-PATENTED, PENDING, ABANDONED

I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

NAME	ATTORNEY/AGENT	REGISTRATION NUMBER	TELEPHONE NUMBER
Yukiko Iwata	Attorney	35,748	(713) 241-5593
NAME	ATTORNEY/AGENT	REGISTRATION NUMBER	TELEPHONE NUMBER
Dean F. Vance	Attorney	27,603	(713) 241-3716

Revised June 1995

SEND CORRESPONDENCE TO:

(NAME) Yukiko Iwata
c/o Shell Oil Company
Intellectual Property
P.O. Box 2463
Houston, TX 77252-2463

DECLARATION AND POWER OF ATTORNEY FOR PATENT APPLICATION

Page 2 of 2
ATTORNEY'S DOCKET NO.
TS0926 (US)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

FULL NAME OF SOLE OR FIRST INVENTOR (given name, family name) Maria Barbara Hendrica VAN CRIJNEN-BEERS	
INVENTOR'S SIGNATURE	DATE SIGNED
RESIDENCE Badhuisweg 3, 1031 CM Amsterdam, The Netherlands	CITIZENSHIP Netherlands
POST OFFICE ADDRESS Badhuisweg 3, 1031 CM Amsterdam, The Netherlands	

FULL NAME OF SECOND JOINT INVENTOR, IF ANY (given name, family name) Jean-Paul DARNANVILLE	
SECOND INVENTOR'S SIGNATURE	DATE SIGNED
RESIDENCE Route de Caen, 76530 Grand Couronne, France	CITIZENSHIP French
POST OFFICE ADDRESS Route de Caen, 76530 Grand Couronne, France	

FULL NAME OF THIRD JOINT INVENTOR, IF ANY (given name, family name) Carolus Matthias Anna Maria MESTERS	
THIRD INVENTOR'S SIGNATURE	DATE SIGNED
RESIDENCE Badhuisweg 3, 1031 CM Amsterdam, The Netherlands	CITIZENSHIP Netherlands
POST OFFICE ADDRESS Badhuisweg 3, 1031 CM Amsterdam, The Netherlands	

FULL NAME OF FOURTH JOINT INVENTOR, IF ANY (given name, family name) Thomas Joris REMANS	
FOURTH INVENTOR'S SIGNATURE	DATE SIGNED
RESIDENCE Badhuisweg 3, 1031 CM Amsterdam, The Netherlands	CITIZENSHIP Belgian
POST OFFICE ADDRESS Badhuisweg 3, 1031 CM Amsterdam, The Netherlands	

FULL NAME OF FIFTH JOINT INVENTOR, IF ANY (given name, family name)	
FIFTH INVENTOR'S SIGNATURE	DATE SIGNED
RESIDENCE	CITIZENSHIP
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